Spin interactions of interstitial Mn ions in ferromagnetic GaMnAs

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The recently reported Rutherford backscattering and particle-induced X-ray emission experiments[1] have revealed that in low-temperature MBE grown $Ga_{1-x}Mn_xAs$ a significant part of the incorporated Mn atoms occupies tetrahedral interstitial sites in the lattice. Here we study the magnetic properties of these interstitial (Mn_I) ions. We show that they do not participate in the hole-induced ferromagnetism. Moreover, Mn_I double donors may form pairs with the nearest substitutional (Mn_{Ga}) acceptors - our calculations evidence that the spins in such pairs are antiferromagnetically coupled by the superexchange. We also show that for the Mn ion in the other, hexagonal, interstitial position (which seems to be the case in the $Ga_{1-x-y}Mn_xBe_yAs$ samples) the p-d interactions with the holes, responsible for the ferromagnetism, are very much suppressed.

The incorporation of transition metal ions into the III-V host semiconductors by low-temperature molecular beam epitaxy (LT MBE), i.e., the discovery of ferromagnetic dilute magnetic semiconductors (DMS) in the pioneering work by Munekata *et al.*[5], was a major step towards the integration of the spin degrees of freedom with the semiconducting properties in the same material. Still, the prospects for practical applications of DMS in "spintronic" devices depend crucially on the possibilities to increase in these materials the temperature of the transition to the ferromagnetic phase. The highest Curie temperatures (T_C) in DMS have been obtained by a substitution of Mn for Ga in GaAs, which was complemented by a post-growth annealing in temperatures only slightly exceeding the LT MBE growth temperature. Until recently the T_C=110 K seemed to be the upper limit for this material[6,7,8,9]. In the last months, however, considerably higher values of T_C in GaMnAs, even exceeding 150 K for thin films, have been reported by several groups[3,10,11,12]. This progress has been made basically by an optimization of the annealing time and temperature.

In the theoretical models describing the ferromagnetism in DMS (e.g., in Ref. 13,14,15) the T_C is expected to increase with both, the magnetic ions and hole concentrations. In LT MBE grown $Ga_{1-x}Mn_xAs$ this was indeed experimentally established for Mn concentrations up to about x=0.07,[6]. The Mn ion in the substitutional position in the GaAs lattice (Mn_{Ga}) acts as an acceptor, but in all $Ga_{1-x}Mn_xAs$ samples the hole concentration is substantially lower than the Mn content. This has been ascribed to the presence of compensating donors, in particular to the formation of arsenic antisites (As_{Ga}) during the epitaxial growth of $Ga_{1-x}Mn_xAs$ at As overpressure[16,17]. In Ref.7,9 and 18 the observed annealing-induced changes of the T_C were attributed solely to the decrease of the concentration of arsenic antisites leading to the increase of the hole concentration. These antisites, however, are relatively stable defects - it was shown that to remove As_{Ga} from LT MBE grown GaAs the annealing temperatures above 450 C are needed[19]. Recently, simultaneous channeling Rutherford backscattering (c-RBS) and particle-induced X-ray emission (c-PIXE) experiments shed new light on this problem[1]. Namely, they have revealed that in LT MBE grown ferromagnetic $Ga_{1-x}Mn_xAs$ with high x a significant fraction of incorporated Mn atoms (ca 15% for the as-grown $Ga_{0.91}Mn_{0.09}As$ sample) occupies well defined, commensurate with the GaAs lattice interstitial positions.

In the diamond cubic crystal lattice there are two possible interstitial positions, the so called tetrahedral and hexagonal sites, in which the atoms are shadowed along $\langle 100\rangle$ and $\langle 111\rangle$ direction and exposed in the $\langle 110\rangle$ axial channel, as seen at the experiment. They can be distinguished by studying angular scans around the $\langle 110\rangle$ axial direction[20]. The scans presented in Ref. 1 suggested that the interstitial Mn ions (Mn_I) observed in $Ga_{1-x}Mn_xAs$ occupy the tetrahedral sites, in which the interstitial is surrounded by four nearest neighbors, as presented in Fig. 1.

The Mn_I serve, like As_{Ga}, as double donors, decreasing the hole concentration. The results presented in Ref. 1 directly showed that in the process of LT annealing the Mn_I ions are moved to random, incommensurate with the GaAs lattice positions (e.g., MnAs clusters), in which the Mn ions are electrically inactive. Thus, in the annealed samples the concentration of the compensating Mn_I donors decreases considerably whereas the hole concentration increases and the observed Curie temperature is much higher. Moreover, it was demonstrated that the appropriate annealing increases the saturation magnetization, i.e., that the presence of Mn_I reduces the net magnetic moment[1,2,3,4].

The described above experimental results stimulated theoretical studies on the formation and properties of interstitial Mn in the GaMnAs ternary compound. First, the electronic structure of the GaMnAs with Mn in substitutional and interstitial position was calculated by *ab initio* methods, showing that indeed Mn interstitials

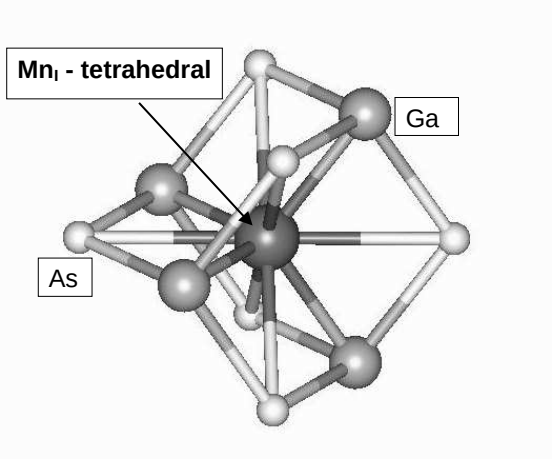

FIG. 1: The nearest four cation and six anion neighbors for an ion in the tetrahedral interstitial position in the zinc-blende lattice.

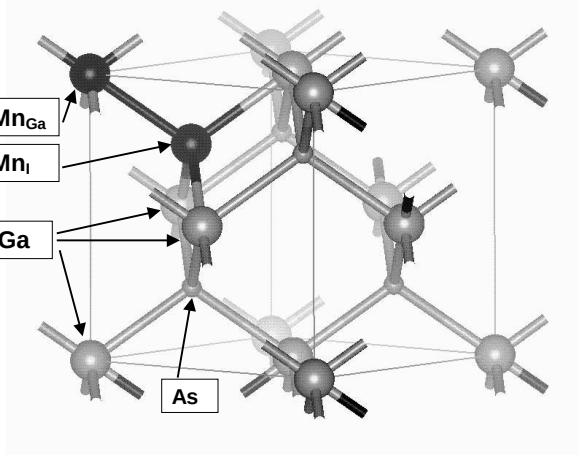

FIG. 2: $Mn_{Ga}-Mn_I$ pair in the GaAs structure.

act as double donors[21]. In a recent paper[22] the self-compensation of Mn in such semiconductors was studied within the density-functional theory. In Ref. 22 it was shown that interstitial Mn can be easily formed near the surface. Here we consider the spin properties of interstitial magnetic ions. We study the spin interactions for the Mn_I ion in the tetraheadral interstitial position in order to provide theoretical basis for the understanding of the experimental findings concerning the magnetic behavior of the as-grown and annealed $Ga_{1-x}Mn_xAs$ samples. We analyze the hybridization of the d-orbitals of these ions with the valence band p-states. This effect is essential for both, the superexchange and the RKKY-type, dominant ion-ion interactions in DMS. It is widely accepted that the latter mechanism is responsible for the hole-induced ferromagnetism in III-V DMS and that the T_C depends crucially on the p-d hybridization - within the Zener model[13] T_C is proportional to the square of the kinetic p-d exchange constant β, i.e., to the fourth power of the hybridization constant V at the centre of the Brillouin zone.

The valence band states in $Ga_{1-x}Mn_xAs$ are built primarily from the anion p-orbitals, thus the p-d hybridization for a given magnetic ion is determined by the positions of its nearest-neighbor anions. In zinc-blende lattice of GaAs, the Mn ion in the cation substitutional position has four anion nearest neighbors at the distances $a\sqrt{3}/4$ (where a is the lattice constant) along the [1, 1, 1], [1,-1,-1], [-1, 1,-1] and [-1,-1, 1] directions. For these positions the inter-atomic matrix elements, $E_{x,xy}$, $E_{x,yz}$, $E_{x,zx}$, etc., expressed in terms of the Harrison parameters $V_{pd\sigma}$ and $V_{pd\pi}$[23], add up constructively to the hybridization constant V in the hybridization Hamiltonian $\hat{H}_h$, with different weights for different points of the Brillouin zone. At the point $\vec{k}$=0 of the Brillouin zone they sum up to the value: $4(V_{pd\sigma} - 2/\sqrt{3}V_{pd\pi})$.

In contrast, the ion in a tetrahedral interstitial position, e.g., $(\frac{1}{4}\frac{1}{4}\frac{3}{4})$ as in Fig. 2, has 6 anion neighbors on [0, 0, ± 1], [0, ± 1, 0] and [±1, 0, 0] directions, at the distances $a/2$ (see Fig. 1). In this case all not equal zero inter-atomic matrix elements are proportional to the appropriate $\sin(ak_i/2)$ (where k_i, $i = x, y, z$, are the components of the wave vector $\vec{k}$) and they vanish at the centre of the Brillouin zone. Thus, the Mn_I d-orbitals do not hybridize with the p-states of the holes at the top of the valence band (i.e. for the tetrahedral interstitials the kinetic exchange constant β_{I_t}= 0) and they do not contribute to the hole-induced ferromagnetism. This means that the formation of Mn interstitials decreases not only the hole concentration but also the number of Mn ions participating in the Zener-type ferromagnetism. Still, these effects do not explain why the removal of interstitials leads to the increase of magnetization and to the higher T_C than expected from the rise of the hole concentration[2].

As pointed out already by Yu *et al.*[1] the electrostatic attraction between positively charged Mn_I donors and negative Mn_{Ga} acceptors stabilizes the otherwise highly mobile Mn_I in the interstitial sites adjacent to Mn_{Ga}, forming a Mn_{Ga}-Mn_I pair, as shown in Fig. 2. One notices that despite the fact that for the interstitials the p-d kinetic exchange and, consequently, the hybridization mediated spin interactions with holes in the vicinity of the top of the valence band vanish, the ionic spins in the pair can be coupled by superexchange mechanism. In the latter process the spins of the two ions, $\vec{S}_1$ and $\vec{S}_2$, are correlated due to the spin-dependent p-d exchange interaction between each of the ions and the valence band electrons in the entire Brillouin zone. The superexchange Hamiltonian:

$$\hat{H}_{superexchange} = -2J(\vec{R}_{12})\hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2 \qquad (1)$$

can be obtained by a proper selection of spin-dependent terms in the matrix of the fourth order perturbation with

respect to the hybridization for a system of two ions in the crystal:

$$-\sum_{l,l',l''}\frac{\langle f\mid \hat{H}_h\mid l''\rangle\langle l''\mid \hat{H}_h\mid l'\rangle\langle l'\mid \hat{H}_h\mid l\rangle\langle l\mid \hat{H}_h\mid i\rangle}{(E_{l''}-E_0)(E_{l'}-E_0)(E_l-E_0)} \tag{2}$$

Using the virtual transition picture, one can say that the superexchange is a result of four virtual transitions of an electron - from the band onto the d-shell of the ion and from the ionic d-shell to the band, in different sequences[24]. The quantitative determination of the superexchange constant J requires the knowledge of the energies of these virtual transitions, which are represented by the energy differences between the intermediate and initial states of the system of two ions and the completely filled valence bands, in the denominator of Equation (2). Of primary importance it is, however, to determine the sign of the superexchange interaction for the Mn_{Ga}-Mn_I pair. In the following, we calculate the exchange constant J within a simplified model, in which we neglect the dispersion of the valence bands but we account for the wave-vector dependence of the hybridization matrix elements. The resulting formula for the exchange constant J reads:

$$J(\vec{R}_{12})=-\frac{1}{25}\left[\frac{1}{E_{a_1}E_{a_2}}\left(\frac{1}{E_{a_1}}+\frac{1}{E_{a_2}}\right)+\frac{1}{E_{a_1}^2(E_{a_1}+E_{d_2})}+\frac{1}{E_{a_2}^2(E_{a_2}+E_{d_1})}\right]\times \tag{3}$$
$$\times\sum_{\nu_1,\nu_2,\vec{k}_1,\vec{k}_2,m,n}V^*_{\nu_1,\vec{k}_1,m}(2)V_{\nu_2,\vec{k}_2,m}(2)V^*_{\nu_2,\vec{k}_2,n}(1)V_{\nu_1,\vec{k}_1,n}(1)$$

In Equation (3) the summation runs over the valence band indices ν_1 and ν_2, the wave-vectors $\vec{k}_1$, $\vec{k}_2$ from the entire Brillouin zone, and over the Mn d-orbitals m, n. The energies E_{a_i} and E_{d_i} (i = 1,2) are the transfer energies for the electron from the valence band onto the ion i ("acceptor") and from the ion i to the valence band ("donor"), respectively. It should be noted that these energies for the interstitial Mn ion are completely unknown. Still, since all these energies as well as the sum, which we calculated numerically, are positive, we can conclude that the Mn_{Ga}-Mn_I pair is *antiferromagnetically* coupled. Thus, Mn ions when in tetrahedral interstitial positions not only do not contribute to the hole-induced ferromagnetism but they also make some of the substitutional Mn ions magnetically inactive by forming with them close pairs, in which the spins of the ions are antiferromagnetically coupled by the superexchange mechanism. This explains the experimental observations that the removal of Mn_I ions by low-temperature annealing leads not only to an increase of the hole concentration, but also to a significant increase of the magnetization.

To estimate the strength of this coupling we compare J with the superexchange constant J' for a Mn_{Ga}-Mn_{Ga} closest pair, obtained within the same simple model. Using the same transition energies for both Mn_{Ga} and Mn_I ions, we obtain $J/J' \approx 1.6$. This is not surprising in view of the small distance between the interstitial and the nearest substitutional Mn ions and the larger number of anion neighbors for Mn_I. With a reasonable value of 3 eV for the Mn_{Ga} charge transfer energies, with the values of Harrison parameters $V_{pd\sigma}$=1.1 eV[25], and $V_{pd\pi}=-\frac{1}{2}V_{pd\sigma}$, (which for the Mn_I we scale according to the Harrison's prescription)[23] the absolute values of J and J' constants are by far not negligible: $J \approx 71$ K and $J' \approx 43$ K.

The role of interstitial Mn ions occurred to be even more pronounced in $Ga_{1-x-y}Mn_xBe_yAs$ samples, grown at Notre Dame with the hope to increase the hole concentration, and hence T_C, by introducing another acceptor[26]. Instead, it turned out that adding Be to $Ga_{1-x}Mn_xAs$ increases the concentration of Mn_I at the expense of Mn_{Ga}[4,27]. At the same time, although the hole concentration does not change significantly, the T_C drops dramatically[26,28], in agreement with the presented above result that the Mn_I do not participate in the hole-induced ferromagnetism. Recently performed angular scans seem to suggest, however, that the Be_{Ga} acceptor stabilizes the Mn interstitial donor not in the tetrahedral but in the hexagonal, ($\frac{3}{8}\frac{5}{8}\frac{3}{8}$) position[29]. In this site the Mn_I has three anion nearest neighbors, as shown in Fig. 3, on the [-1, -3, -1], [3, 1, -1] and [-1, 1, 3] directions, at the distance $a\sqrt{11}/8$. In such case one does not expect the kinetic p-d exchange constant β to be equal to zero - it can be rather expected that the hybridization for the ion in this site should be stronger, due to the smaller distance to the anions, what increases the Harrison parameters $V_{pd\sigma}$ and $V_{pd\pi}$). Surprisingly enough, the most of the interatomic matrix elements in the hybridization constant V for the hexagonal interstitial Mn mutually cancel at the centre of the Brillouin zone. This leads to a considerably smaller than for the substitutional Mn ion value of the kinetic exchange constant β_{I_h}, i.e., $\beta/\beta_{I_h} \approx 5$. As the Curie temperature in the Zener model depends on β^2, we conclude that the contribution to the hole-induced ferromagnetism from the Mn ions occupying the hexagonal interstitial sites is as well very much suppressed.

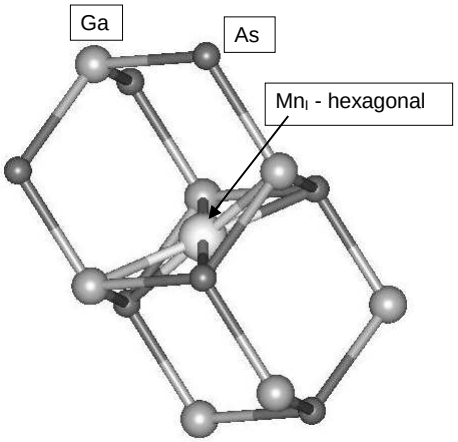

FIG. 3: The six (three cations and three anions) nearest neighbors and the next four cations and four anions for an ion in the hexagonal interstitial position in the zinc blende lattice.

In conclusion, we have shown that not only the compensating properties of the interstitial magnetic ions impose a limit to the Curie temperature in the ferromagnetic $Ga_{1-x}Mn_xAs$ and $Ga_{1-x-y}Mn_xBe_yAs$ samples. Also their magnetic properties in both (tetrahedral and hexagonal) interstitial sites, i.e., the negligible kinetic exchange constant and strong antiferromagnetic superexchange with the adjacent substitutional Mn ion, act towards diminishing the transition temperature.

Acknowledgments

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